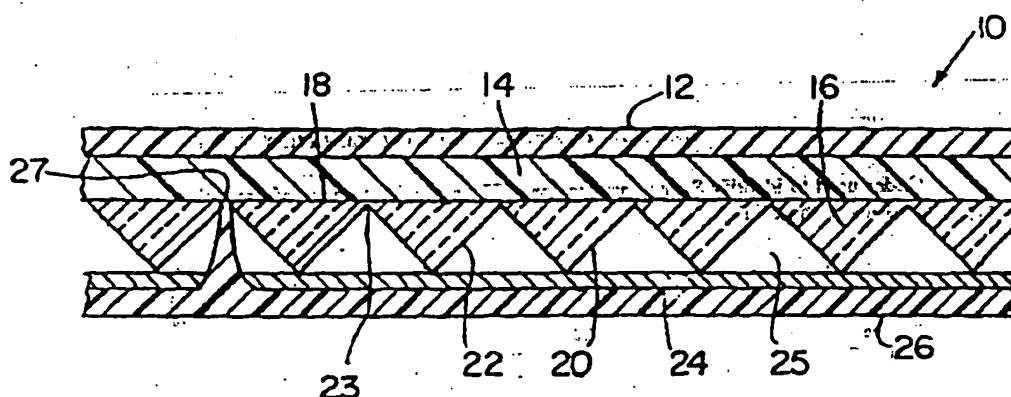




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B32B 27/08, 3/28, A62B 17/00, G02B 5/124	A1	(11) International Publication Number: WO 95/07179 (43) International Publication Date: 16 March 1995 (16.03.95)
(21) International Application Number: PCT/US94/10036 (22) International Filing Date: 8 September 1994 (08.09.94) (30) Priority Data: 08/119,459 10 September 1993 (10.09.93) US (71) Applicant: REFLEXITE CORPORATION [US/US]; Reflexite Technology Center, 120 Darling Drive, Avon, CT 06001-4217 (US). (72) Inventor: MARTIN, David, C.; 114 Worthington Pt. Road, Berlin, CT 06037 (US). (74) Agents: REYNOLDS, Leo, R. et al.; Hamilton, Brook, Smith & Reynolds, Two Militia Drive, Lexington, MA 02173 (US).		(81) Designated States: CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.

(54) Title: A FIRE-RESISTANT, RETROREFLECTIVE STRUCTURE



(57) Abstract

A fire-resistant retroreflective structure having an array of rigid retroreflective elements and a method for making the structure are disclosed. The retroreflective structure is formed of an array of rigid retroreflective elements having a first side and a second side. A transparent polymeric film is attached to the first side of the array of rigid retroreflective elements. A transparent fire-resistant outer layer is attached to the transparent polymeric film. A flame-retardant layer is placed proximate to the second side of the array of rigid retroreflective elements. A fire-resistant polymer underlayer is attached to the flame-retardant layer. The fire-resistant polymer underlayer can be bonded to the transparent polymeric film through the array of rigid retroreflective elements and the flame-retardant layer.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Macritonia
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Benin	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Cote d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

A FIRE-RESISTANT, RETROREFLECTIVE STRUCTUREBackground of the Invention

Retroreflective materials are employed for various safety purposes. Particularly, these materials are
5 useful at night time when visibility is critical under low light conditions. This is especially important for firemen's coats and protective clothing where visibility is important. However, the conditions that firemen are exposed to are exceedingly harsh,
10 especially in regard to excessive heat and temperature conditions. Many retroreflective materials are made of plastics that soften at temperatures of about 212°F (100°C). The softened plastic in such materials begins to flow causing the material to lose its
15 retroreflectivity.

The clothing and any trim on the clothing for firemen must meet standards established by the National Fire Protection Association (NFPA). The NFPA has recently proposed a new and stricter standard, entitled
20 "Standard on Protective Clothing for Structure Fire Fighting No. 531." This proposed standard requires that the outerlayer material of the fire fighting protective coating pass a set of laboratory test conditions which include flame resistance, heat
25 resistance, fluorescence, photometry, and seam strength. In the test for heat resistance, test materials are placed in a forced convection oven at a temperature of 500°F (260°C) for a period of at least five minutes. During the test, the materials must not
30 melt, separate, or ignite. In the test for flame resistance, the test material is exposed to a direct

-2-

flame of a bunsen burner for twelve seconds. During this time, the test material must char less than four inches (10 cm) while not dripping or melting during exposure to the flame. Further, once the flame is
5 turned off, the test material must have an afterflame of less than two seconds. A structure that meets these standards with respect to flame retardance, which is defined as the resistance to catching fire when exposed to a direct flame, and heat resistance, which is
10 defined as the resistance to melting, separating, or igniting when exposed to substantial heat, is hereinafter considered a fire-resistant structure.

This proposed standard further requires that the firemen's coats be trimmed with 325 square inches (2097
15 cm²) of a retroreflective tape which meets the standard. The tape is applied in the form of bands around the sleeves and on the bottom of the coat.

One type of retroreflective material is formed of cube-corner or prism retroreflectors, such reflectors,
20 are described in U.S. Patent 3,712,706, issued to Stamm (January 23, 1973). Generally, the prisms are made by forming a master dye on a flat surface of a metal plate or other suitable material. To form the cube corners, three series of parallel equidistance intersecting
25 v-shaped grooves at 60° angles to each other are inscribed in the flat plate. The die is then used to form the desired cube-corner array into a flat plastic surface. When the groove angle is 70 degrees, 31
30 minutes, 43.6 seconds, the angle formed by the intersection of two cube faces (the dihedral angle) is

-3-

90 degrees, and the incident light is retroreflected back to the source.

The efficiency of a retroreflective structure is a measure of the amount of incident light returned within
5 a cone diverging from the axis of retroreflection.

Distortion of the prism structure adversely affects the efficiency. Furthermore, cube-corner retroreflective elements have low angularity, i.e., the elements will only brightly reflect light that impinges on it within
10 a narrow angular range centering approximately on its axis of retroreflection. Low angularity arises from the inherent nature of these elements which are trihedral structures having three mutually perpendicular lateral faces. The elements are arranged
15 so that the light to be retroreflected impinges into the internal space defined by the faces, and retroreflection of the impinging light occurs by total internal reflection of the light from face to face of the element. Impinging light that is inclined
20 substantially away from the axis of retroreflection of the element (which is the trisector of the internal space defined by the faces of the element) strikes the face at an angle less than its critical angle, thereby passing through the face rather than being reflected.

25 Further details concerning the structures and the operation of cube-corner microprisms can be found in U.S. Patent 3,684,348, issued to Rowland (August 15, 1972), incorporated in its entirety by reference herein. A method for making retroreflective sheeting
30 is also disclosed in U.S. Patent 3,689,346, issued to Rowland (September 5, 1972), also incorporated by

-4-

reference herein. The method disclosed in U.S. Patent 3,689,346, teaches forming cube-corner microprisms in a cooperatively configured mold. The prisms are bonded to sheeting to form a composite structure in which the cube-corner formations project from one surface of the sheeting.

Summary of the Invention

A need exists for retroreflective structures that can be heated to a temperature of about 500°F (260°C) for more than five minutes while not significantly diminishing its fire-resistant properties.

The present invention relates to a fire-resistant retroreflective structure which includes an array of rigid retroreflective elements having a first side and a second side. A transparent polymeric film is attached to the first side of the array of the rigid retroreflective elements. A transparent fire-resistant polymer outerlayer is attached to the transparent polymeric film. A flame-retardant layer is proximate to the second side of the array of rigid retroreflective elements. A fire-resistant underlayer is attached to the flame-retardant layer. The transparent polymeric film can be bonded to the fire-resistant underlayer through the array of rigid retroreflective elements and the flame-retardant layer.

A method for forming a fire-resistant retroreflective structure includes the steps of providing a transparent fire-resistant polymer film. A transparent polymeric film is applied to the transparent fire-resistant polymer film. A polymerizable material is polymerized in a suitable

-5-

mold to form a rigid retroreflective array of rigid elements having a first side and second side. The first side of the rigid retroreflective array is applied to the transparent polymeric layer. A flame-retardant layer is placed proximate to the second side of the rigid retroreflective array. A fire-resistant underlayer is applied to the flame-retardant layer, thereby forming a fire-resistant, retroreflective structure. The transparent polymeric film is bonded to the fire-resistant underlayer through the array of rigid retroreflective elements and the flame-retardant layer.

This invention includes many advantages. One advantage is that traditional colored transparent vinyl plastics can be used as retroreflective substrates while the retroreflective structure can meet the proposed 500°F (260°C) exposure requirement without melting, dripping, charring or retaining enough heat energy so as to inflict a serious burn on a fire fighter. The configuration of the retroreflective structure decreases the mass of the vinyl thermoplastic sufficiently to minimize the exposure of the vinyl to heat during the 500°F (260°C) test. Another advantage is that the tape retains a significant portion of its retroreflectivity after exposure to a temperature of 425-450°F (218-232°C). Further, the surface of the structure is resistant to solvents and wetting, and can be easily cleaned to remove soot and dirt, while the structure retains its retroreflectivity.

-6-

Brief Description of the Drawing

Figure 1A is a cross-sectional view of a first embodiment of a retroreflective structure of the present invention.

5 Figure 1B is a top view of the first embodiment of a retroreflective structure of the present invention.

Figure 2 is a cross-sectional view of a second embodiment of a retroreflective structure of the present invention having a retroreflective coating.

10 Figure 3 is a cross-sectional view of a third embodiment of a retroreflective structure of the present invention having a retroreflective coating.

Figures 4A, 4B, 4C, 4D, 4E, 4F, and 4G are cross-sectional views of a method for forming a
15 retroreflective structure at various points in forming an embodiment of the present invention.

Detailed Description of the Invention

The features and other details of the method and apparatus of the invention will now be more
20 particularly described with reference to the accompanying drawings and pointed out in the claims. The same numeral presented in different figures represent the same item. It will be understood that the particular embodiments of the invention are shown
25 by way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. All parts and percentages are by weight unless otherwise
30 specified.

-7-

One embodiment of the invention, as shown in Figure 1A in a cross-sectional view, is retroreflective structure 10. Retroreflective structure 10 is formed of an outerlayer 12 having, inter alia, the following properties comprised in a fire-resistant polymer that does not significantly char, melt or ignite when exposed to a temperature of 500°F (260°C) in hot air for at least five minutes. Further, outerlayer 12 does not significantly burn when exposed to a direct flame as required by NFPA Standard 531. Outerlayer 12 provides an abrasion, soil, and solvent resistant surface for retroreflective structure 10 which is transparent to visible light while not reducing or interfering with the reflective or optical performance. The outerlayer 12 provides a surface that can be readily cleaned of soot, dirt, solvents, inks, etc. including materials that are considered indelible on cloth. Typically, the outerlayer is readily cleaned by wiping with a tissue, rinsing with water, or washing with a mild soap and water. In addition, outerlayer 12 allows the retroreflective structure to retain essentially all of its retroreflectivity when sprayed with droplets of water or covered with a mist. Furthermore, outerlayer 12 essentially eliminates the migration of fluorescent colorant from retroreflective structure 10 and reduces the frictional and cling qualities that plasticized vinyl possesses.

Outerlayer 12 is composed of a suitable polymer that is crosslinked and carbonizes at a temperature higher than a vinyl plastic. Alternatively, outerlayer 12 can be a copolymer. These polymers include a

-8-

polyamide, polyester, polyacrylic, polyurethane or other ultraviolet-cured coatings that polymerize and crosslink. The polymer is substantially as flexible as the other layers that are included in the retroreflective structure. In a preferred embodiment, the polymer is a transparent polyurethane film available from Sancor Corp. under the trademark of Sancor™ 815.

Outerlayer 12 can have a thickness in the range of between about 0.0001 and 0.0004 inches (0.00025 and 0.001 cm). In a preferred embodiment, the thickness is in the range of between about 0.0002 and 0.0003 inches (0.0005 and 0.00076 cm). The selected thickness is dependent upon the method of fabrication, the polymer, and the fire-resistant characteristics desired for the retroreflective structure.

Outerlayer 12 and transparent film 14 are bonded together. Transparent film 14 can be comprised of a transparent thermoplastic vinyl plastic film, such as polyvinyl chloride, polyvinylidene chloride, urethane films etc. which are extensible and flexible. Transparent film 14 is transparent to visible light and can be either clear or colored. Suitable colors include fluorescent orange, yellow, etc. In a preferred embodiment, the transparent film is a fluorescent lime-green in color. An example of a suitable transparent film 14 is a polyvinyl chloride film available from Renoliot Corp. under the trademark Renoliot™ H1W series. Outerlayer 12 and transparent film 14 are bonded by many suitable techniques, such as

-9-

by an adhesive, ultrasonic welding, casting directly onto the outerlayer, etc.

Transparent film 14 can have a thickness in the range of between about 0.003 and 0.02 inches (0.0076 and 0.051 cm). In a preferred embodiment, the thickness is in the range of between about 0.006 and 0.01 inches (0.015 and 0.025 cm). The selected thickness is dependent upon the method of fabrication, the thermoplastic selected, and the characteristics desired for the retroreflective structure.

The retroreflective array 16 is an optical element that can consist of retroreflective cube-corner prism elements. Other retroreflective arrays include fresnel lenses and glass beads. The retroreflective array 16 has a first side 18 and second side 20. Retroreflective array 16 can be formed of a transparent polymer that is selected from a wide variety of polymers that are considered rigid or hard. These polymers include the polymers of urethane, acrylic acid esters, hard epoxy acrylates, etc. Other polymers include polycarbonates, polyesters, polynitriles, polyolefins, acrylated silanes, and urethane acrylates. The retroreflective array 16 is attached by a suitable deposition process, such as by ultraviolet light, an adhesive, radio frequency welding or election beam. Preferably, the polymer is cast in a mold for forming an array of rigid retroreflective elements with a monomer or oligomer, and polymerization is initiated by ultraviolet radiation. Transparent film 14 provides a transparent substrate to retroreflective array 16 which

-10-

provides a smooth surface upon which retroreflective array 16 is attached.

5 The thickness of retroreflective array 16 at valley 23, where the cube-side edges 22 intersect, is sufficiently thin so that non-extensible prism array 16 can crack and split along valley 23 when a minimal force is applied to retroreflective structure 10. This allows retroreflective structure 10 to significantly flex while allowing the elements of retroreflective
10 array to remain in position with respect to transparent film 14, where retroreflective array 16 is attached, whereby retroreflection is not significantly distorted, thereby significantly maintaining the retroreflective properties of retroreflective structure 10.

15 The retroreflective cube-corner prism elements can have a length along each cube-side edge 22 in the range of between about 0.003 and 0.006 inches (0.0076 and 0.015 cm). In one embodiment, each cube-side edge 22 has a length of about 0.0049 inches (0.012 cm).

20 Proximate to the second side of retroreflective array 16 is flame-retardant layer 24 having air space 25 disposed therebetween. Airspace 25 is considered the open seal area. Flame-retardant layer 24 is comprised of a suitable material which contains
25 sufficient flame-retardant to reduce the flammability of the retroreflective structure 10. Typically, flame-retardant layer 24 is comprised of a carrying base, such as a rubber-based adhesive. A preferred adhesive is Bostik 4050 available from Bostik Corp., and a
30 flame-retardant composition, such as a brominated flame-retardant compound. One such brominated

-11-

substance is available from Great Lakes Corp. under the trademark Great Lakes DE-83R™. In a preferred embodiment, the flame-retardant layer is comprised of about 60.23% Bostik 4050, 31.32% Great Lakes DE-83R™ and 8.45% xylene. The thickness of flame-retardant layer 24 can be in the range of between about 0.0002 and 0.004 inches (0.0005 and 0.01 cm). In a preferred embodiment, the thickness is in the range of between about 0.002 and 0.0022 inches (0.0051 and 0.0056 cm). The selected thickness is dependent upon the method of fabrication, the flame-retardant selected along with the carrying base, such as the rubber adhesive, and the characteristics required for the retroreflective structure.

Underlayer 26 is comprised of a fire-resistant material. This material can include a polymer, such as a polyamide, or a glass fiber. Other suitable materials include a fiberglass-reinforced vinyl mesh or weave, laminated vinyls or other similar backings. In a preferred embodiment, underlayer 26 is a fire-resistant vinyl, fiberglass reinforced web available from Cooley Corporation, Model No. FT-12-U.

Underlayer 26 can have a thickness in the range of between about 0.003 and 0.005 inches (0.0076 and 0.013 cm). In a preferred embodiment, the thickness is about 0.004 inches (0.01 cm). The selected thickness is dependent upon the method of fabrication, the polymer selected, and the characteristics desired for the retroreflective structure.

Underlayer 26 is bonded to transparent film 14 through retroreflective array 16 and flame-retardant

-12-

layer 24 at point 27. As shown in a top view of retroreflective structure 10 in Figure 1B, grid pattern 28 can be formed in retroreflective structure 10 by a mold having a mirror image of the grid pattern. While
5 applying pressure to retroreflective structure 10, the structure is exposed to a suitable energy source such as ultraviolet light, heat or electron beam. The portion of retroreflective structure, which is not bonded between transparent layer 14 and underlayer 26,
10 forms air space 25 between retroreflective array 16 and flame-retardant layer 24. In a preferred embodiment, the lines of the grid are spaced about a half inch (1.25 cm) or inch apart (2.5 cm) and have a width in the range of between about a sixteenth to an eighth of
15 an inch (0.16 - 0.32 cm). Lines 31 of grid pattern 28 are significantly non-retroreflective as compared to the remainder of retroreflective structure 10.

Figure 2 illustrates another embodiment of the invention. The structure of Figure 2 has many of the
20 same elements of Figure 1 and like elements are designated with the like numerals.

Transparent film 14 with retroreflective array 16 can be laminated to transparent film 14 with a transparent adhesive 29. Transparent adhesive 29
25 provides an adhesive coating that bonds to transparent film 14 and provides crosslinking to anchor retroreflective array 16. The transparent adhesive provides a shield against any plasticizers present in retroreflective structure 10 that would migrate from
30 non-plasticizer resistant oligomers, such as transparent film 14. Plasticizers can have a negative

-13-

effect on the long-term brightness and stability of retroreflective array 16. Alternatively, retroreflective array 16 can be directly cast onto transparent vinyl film 14 in one step.

5 If transparent adhesive 29 is employed to attach flame-retardant layer 24 to the retroreflective array second side 20, transparent adhesive 29 can cause the surface of second side 22 of the retroreflective array 16 to wet, thereby destroying the air interface and
10 eliminating the ability of the array to retroreflect. As a result, retroreflective coating 33 is deposited on the surface of second side 20. Typically, the retroreflective coating is formed by sputtering aluminum, copper, silver or gold or by vacuum
15 metallization. Alternatively, metal lacquers, dielectric coatings and other specular coating materials can be employed.

Figure 3 illustrates another embodiment of the invention. The structure of Figure 3 has many of the
20 same elements of Figure 1 and like elements are designated with the like numerals.

Flame-retardant layer 24, as described in Figure 1, can be a composite of two or more layers. In Figure 3, the flame-retardant layer is composed of a first
25 layer 30, which is attached to retroreflective array 16, a second layer 32, which is attached to first layer 30, and a third layer 34 which is attached to second layer 32. First layer 30 is comprised of a suitable material which contains sufficient flame-retardant to
30 reduce the flammability of retroreflective structure 10. First layer 30 can include a rubber-based adhesive

-14-

with a flame-retardant composition as described above as flame-retardant layer 24. The thickness of the first layer 30 is in the range of between about 0.0004 and 0.0006 inches (0.001 and 0.0015 cm). In a preferred embodiment, the thickness is about 0.0007 inches (0.0018 cm). The thickness selected is dependent upon the method of fabrication, the flame-retardant carrying base combination, and the characteristics required for the retroreflective structure.

Second layer 32 is a thermoplastic to provide structural support with a flame-retardant embedded within it. In one embodiment, the thermoplastic is trikresyl phosphate polyvinyl chloride. The thickness of second layer 32 is in the range of between about 0.005 and 0.015 inches (0.013 and 0.038 cm) and with a preferred thickness of about 0.01 inches (0.025 cm).

Third layer 34 is similar to first layer 30 in composition and size. In one embodiment, third layer 30 includes Bostik 4050 rubber-based adhesive with a brominated flame-retardant with a thickness of about 0.0007 inches (0.0018 cm).

The retroreflective structure can be attached to a suitable article of clothing, such as a fireman's overcoat or other structure, such as a fire helmet or air tank, by means known in the art. For instance, a retroreflective structure can be attached by an adhesive that is plasticizer resistant and that is heat activated or pressure sensitive. Alternatively, it can be sewed onto clothing.

-15-

In Figures 4A, 4B, 4C, 4D, 4E, 4F, and 4G a method for forming an embodiment of fire-resistant retroreflective structure 10 is shown at various points in the process of forming the structure. In Figure 4A, carrier film 36 is attached to outerlayer 12 to provide stability to outerlayer 12 during the formation of retroreflective structure. The carrier film can be formed of polyester, polyamide or any other polymer that is significantly non-extensible and is applied to the other side of outerlayer 12 by a suitable carrier film adhesive 38, such as Q2-7406 available from Dow Chemical Co. The carrier film 36 and the carrier film adhesive 38 are removable from the outerlayer by suitable means upon formation of retroreflective structure 10. Carrier film 36 helps to prevent stretching during the coating and minimizes orientation sensitivity of retroreflective structure 10 when cast and stripped from the mold. The carrier film adhesive can be a temporary adhesive that is thermally stable to degradation when exposed to the temperatures encountered while forming the retroreflective structure. In one embodiment, the carrier film adhesive has a strength in the range of about 180 to 220 grams when subjected to a 180° peeling test. In Figure 4B, the method includes applying transparent film 14 to outerlayer 12 by bonding with an adhesive, ultrasonic welding or by directly casting onto the outerlayer.

In Figure 4C, retroreflective array 16 is formed by casting onto transparent film 14. The retroreflective array has first side 18 and second side 20. Retroreflective array 16 is formed of a polymer,

-16-

such as polyacrylic. The retroreflective array is essentially of the same shape and dimensions as described in Figure 1. Alternatively, first side 18 of retroreflective array 16 is applied to transparent film 14 by a suitable deposition method. Transparent adhesive 29, such as Bostik 7650, can be applied between transparent film 14 and retroreflective array 16.

In Figure 4D, flame-retardant layer 24 is applied to underlayer 26 to form underlayer structure. Flame-retardant layer 24 is allowed to cure if it is rubber-based adhesive flame-retardant layer, as described above. Fire-resistant polymer underlayer 26, such as Cooley FT-12-U, can be heat sealed at 230°F (110°C) to the flame-retardant layer.

In Figure 4E, flame-retardant layer 24 is placed adjacent to retroreflective array 16. Air space 25 is formed between retroreflective array 16 and flame-retardant layer 24 where transparent layer 14 is not bonded to underlayer 26. In Figure 4F, transparent layer 14 and underlayer 26 are bonded at points 27 by placing in a mold having a grid pattern by applying pressure and exposing points 27 to heat, ultraviolet light, etc. to form the bond. Air space 25 is formed between retroreflective array 16 and flame-retardant layer 24 where transparent layer 14 is not bonded to underlayer 26. In Figure 4G, carrier film 36 and carrier film adhesive 38 may be removed from retroreflective array by peeling or other suitable method, thereby forming a fire-resistant retroreflective structure 10.

-17-

Example 1

Fire-resistant retroreflective structure 10 was formed of a hard polyurethane outerlayer having a thickness of 0.003 inches (0.0076 cm) and was made of Sancor™ 815. A transparent film layer was attached to the outerlayer. The film was made of transparent polyvinyl chloride film having a lime color. The film was Renoliot™ H1W having a thickness of 0.006 inches (0.015 cm).

The retroreflective array with a first side and a second side was composed of a transparent ultraviolet cured polyurethane. The prisms had a side length of 0.0049 inches (0.012 cm). A flame-retardant layer was placed proximate to the second side of the retroreflective array.

The flame-retardant layer was comprised of 60.23% rubber-based adhesive Bostik 4050, 31.32% a brominated flame-retardant, Great Lakes DE-83R™, and 8.45% xylene. The flame-retardant layer, which was adjacent to the second side of retroreflective array, had a thickness of 0.0022 inches (0.0056 cm). The underlayer was comprised of a fiberglass reinforced vinyl film, Cooley FT-12-U, and had a thickness of 0.01 inches (0.025 cm).

Samples of the fire-resistant retroreflective structure, two by twelve inches (5.1 by 30.5 cm) in size, were tested for flame retardation and retention of retroreflectivity in specific intensity per unit area at 0 and 90° orientations. The lime colored samples were tested under the methods provided in proposed NFPA Standard on Protective Clothing for Structure Fire Fighting No. 531. The samples were

-18-

tested for retroreflectivity after exposure in a force convection oven for five minutes to various temperatures in the range of between 325 and 500°F (163 and 260°C). After each test, the following were tested: color, strength of the tape maintained in resisting elongation as a percentage of a control sample not exposed to the heating, drip and surface tackiness. The results are disclosed in Table 1.

TABLE 1

10	<u>Temperature</u>		<u>Specific Intensity</u>	<u>Color</u>	<u>Strength</u>
	<u>°F</u>	<u>°C</u>	<u>per Area*</u>		<u>%</u>
	325	163	473 x 440	No change	100
	350	177	423 x 388	Slight Tint	100
	375	191	260 x 220	More Tint	100
15	400	204	82 x 88	Brown Tint	100
	425	218	63 x 62	Dark Brown Tint	100
	450	232	52 x 54	Orange Tint	100
	475	246	7 x 10	Dark Maroon	90
	500	260	1 x 3	Red/Black	80

20 * Specific intensity per unit area in candela/lux/m² measured at 0° and 90°. respectively.

No dripping or surface tackiness was detected. An afterflame burn test measured 1.4 to 1.8 seconds. A burn through of 1.5 inches (3.81 cm) was measured.

25 There was no afterglow detected. The char-length was 0.375 inches (0.95 cm).

-19-

Example 2

Samples of the fire-resistant retroreflective structure, two by twelve inches (5.1 by 30.5 cm) in size, were also tested under British Flame Test Standards prEN 532 (1993) for flammability using a flame application time of ten seconds. The results were assessed against the requirements of Paragraph 6.1 for flame spread under prEN 469 "Protective Clothing for Fire Fighters" (June 1992 version). Five specimens, two by twelve inches (5.1 by 30.5 cm), were tested. The retroreflective samples were washed for five cycles of ISO 6330 at 60°C followed by tumble drying prior to testing. The samples were tested for fluorescence black light activation after exposure in a forced convection oven for five minutes at various temperatures in the range of between 325 and 500°F (163 and 260°C). The results are disclosed in Tables 2 and 3.

-20-

TABLE 2

FLUORESCENCE

(after five minutes at °F)

	<u>Temperature °F</u>	<u>°C</u>	<u>Black Light Activation</u>
5	325	163	unaffected open seal area
	350	177	unaffected open seal area
	375	191	unaffected open seal area
	400	204	unaffected open seal area
	425	218	high level open seal area
10	450	232	reduced level open seal area
	475	246	detectable with black light
	500	260	undetectable with black light

TABLE 3

	<u>TEST</u>	<u>SPECIMEN</u>				
		1	2	3	4	5
15	Flaming to Edge	none	none	none	none	none
	Hole Formation	none	none	none	none	none
	Flaming or Molten					
	Debris	none	none	none	none	none
20	Afterglow Spreads	none	none	none	none	none
	Afterflame time,					
	seconds	1.0	0	0	0	0
	Afterglow,					
	seconds	0	0	0	0	0

-21-

No flaming to edge, hole formation by the flame, flaming or molten debris, or afterglow spread was detected. An afterflame burn test measured an average of 0.5 seconds. There was no afterglow measured.

- 5 The samples met the British standard that requires that no specimen have flaming at the top or side edges, have hole formation, or flaming or molten debris. The mean value of the afterflame test is to be less than or equal to two second, and the mean value of afterglow
10 shall be less than or equal to two seconds. All the tested samples met the British standard.

Equivalents

- 15 Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the claims.

-22-

CLAIMS

1. A fire-resistant, retroreflective structure having an array of elements, comprising:
 - 5 a) an array of rigid retroreflective elements having a first side and a second side;
 - b) a transparent polymeric film attached to the first side of the array of rigid retroreflective elements;
 - 10 c) a transparent fire-resistant polymer outerlayer attached to the transparent polymeric film;
 - d) a flame-retardant layer which is attached to the second side of the array of rigid retroreflective elements; and
 - 15 e) a fire-resistant underlayer attached to the flame-retardant layer.
2. The retroreflective structure of Claim 1 wherein the transparent polymeric film is bonded to the fire-resistant underlayer through the array of
20 rigid retroreflective elements and the flame-retardant layer.
3. The retroreflective structure of Claim 2 wherein the outerlayer includes a crosslinked polyurethane film.
- 25 4. The retroreflective structure of Claim 3 wherein the transparent polymeric film is a polyvinyl film.

-23-

5. The retroreflective structure of Claim 4 wherein the vinyl film is polyvinyl chloride.
6. The retroreflective structure of Claim 5 wherein the polyvinyl chloride contains a colorant.
- 5 7. The retroreflective structure of Claim 6 wherein the colorant is lime in color.
8. The retroreflective structure of Claim 7 wherein the array of rigid retroreflective elements is formed of material selected from a group
10 comprising of hard epoxy polyacrylates, urethanes, polynitriles, polycarbonates, polyesters, and polyolefin.
9. The retroreflective structure of Claim 8 wherein the array of rigid retroreflective elements is
15 formed of a copolymer.
10. The retroreflective structure of Claim 9 wherein the flame-retardant layer includes a brominated flame-retardant.
11. The retroreflective structure of Claim 10 wherein
20 the flame-retardant layer includes a mixture a brominated flame-retardant and an adhesive.
12. The retroreflective structure of Claim 10 wherein the fire-resistant underlayer is a polyamide film.

-24-

13. The retroreflective structure of Claim 10 wherein the fire-resistant underlayer is a fiberglass reinforced vinyl film.
- 5 14. The retroreflective structure of Claim 1 wherein a metallized reflective layer is formed of a metal selected from a group comprising of aluminum, copper, silver, and gold which is deposited on the second side of the rigid retroreflective array.
- 10 15. The retroreflective structure of Claim 14 wherein the metallized reflective layer is bonded to flame-retardant layer by an adhesive.
- 15 16. The retroreflective structure of Claim 1 wherein the transparent polymeric film and the array of rigid retroreflective elements are attached by an adhesive.
17. The retroreflective structure of Claim 1 wherein the surface of the transparent fire-resistant polymer outlet can be readily cleaned.
- 20 18. The retroreflective structure of Claim 1 wherein the structure retains essentially all of its retroreflectivity when sprayed with droplets of water.

-25-

19. A fire-resistant retroreflective structure, comprising:
- a) an array of rigid retroreflective elements having a first side and a second side;
 - 5 b) a transparent polymeric film attached to the first side of the array of rigid retroreflective elements;
 - c) a transparent fire-resistant polymer outerlayer which is attached to the transparent polymeric film;
 - 10 d) a first flame-retardant layer which is attached to the second side of the array of rigid retroreflective elements;
 - e) a second flame-retardant layer which is attached to the first flame-retardant layer;
 - 15 g) a third flame-retardant layer which is attached to the second flame-retardant layer; and
 - h) a fire-resistant polymer underlayer which is attached to the third flame-retardant layer.
 - 20
20. The retroreflective structure of Claim 19 wherein the first flame-retardant layer includes a brominated flame-retardant contained in a rubber-based adhesive film.
- 25 21. The retroreflective structure of Claim 20 wherein the second flame-retardant layer includes trikresyl phosphate in a polyvinyl chloride film.

-26-

22. The retroreflective structure of Claim 21 wherein the third flame-retardant layer includes a brominated flame-retardant contained in a rubber-based adhesive film.

5 23. In a retroreflective structure having a transparent polymeric film and an array of rigid retroreflective elements having a first side and a second side where the transparent polymeric film is attached to the first side of the array of
10 rigid retroreflective elements:

the improvement comprising a transparent fire-resistant polymer outerlayer attached to the transparent polymeric film and a flame-retardant layer which is attached to the
15 second side of the array of rigid retroreflective elements and a fire-resistant polymer underlayer which is attached to the flame-retardant layer, whereby the transparent fire-resistant polymer
20 outerlayer, the flame-retardant layer and the fire-resistant underlayer are sufficient to prevent significant charring, melting and ignition of the retroreflective structure when the structure is exposed to a
25 temperature of about 500°F (260°C) for at least five minutes.

-27-

24. A method for forming a fire-resistant retroreflective structure, comprising the steps of:

- 5 a) providing a transparent fire-resistant polymer film;
- b) applying a transparent polymeric film to the transparent fire-resistant polymer film;
- c) polymerizing a polymerizable material in a
10 suitable mold to form a retroreflective array of rigid elements having a first side and second side;
- d) applying the first side of the retroreflective array to the transparent polymeric layer;
- 15 e) providing a fire-resistant polymer underlayer; and
- f) applying a flame-retardant layer to the fire-resistant polymer underlayer; and
- g) attaching the flame-retardant layer to the
20 second side of the retroreflective array, thereby forming a fire resistant retroreflective structure.

25. The method of Claim 24 wherein a portion of the underlayer is bonded after step g to the
25 transparent polymeric film through the retroreflective array and the fire-resistant polymer underlayer.

-28-

26. The method of Claim 24 wherein an adhesive coating is applied between steps b and c to the transparent polymeric film.
- 5 27. The method of Claim 24 wherein a metallization layer is applied between steps d and e to the second side of the retroreflective array.
- 10 28. The method of Claim 26 wherein an adhesive is applied between steps f and g to the metallization layer.
-

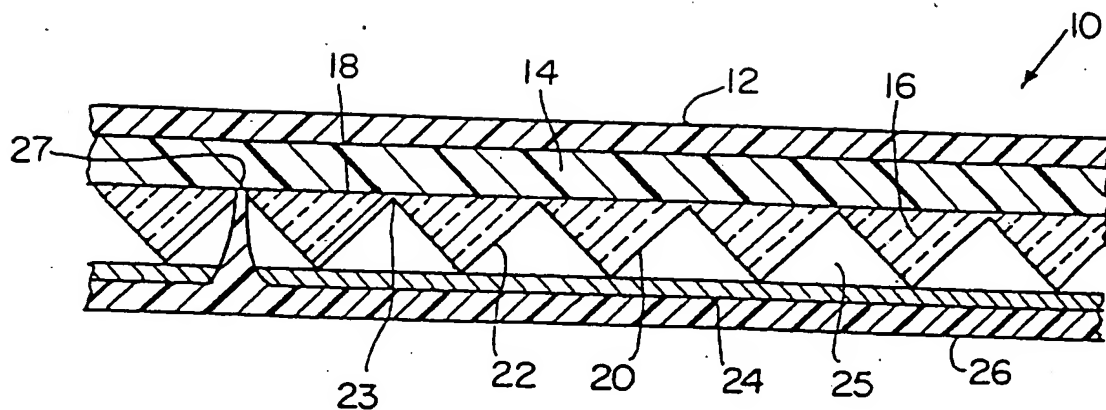


FIG. 1A

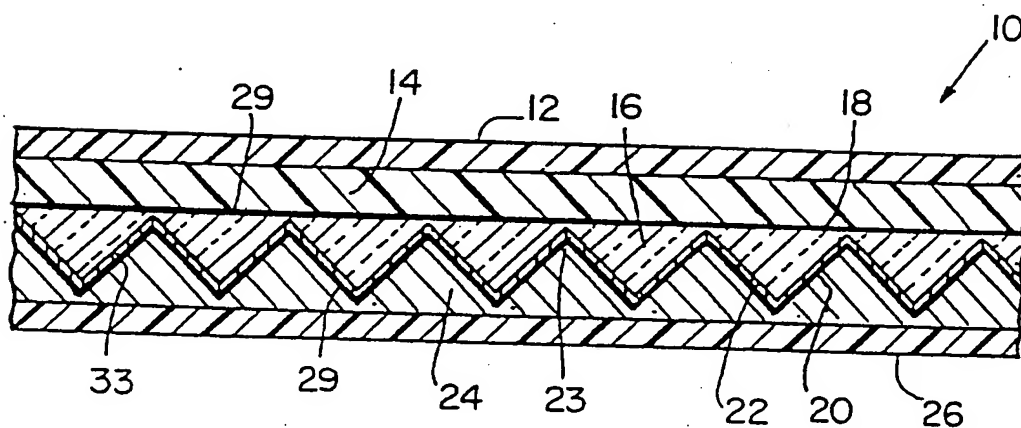


FIG. 2

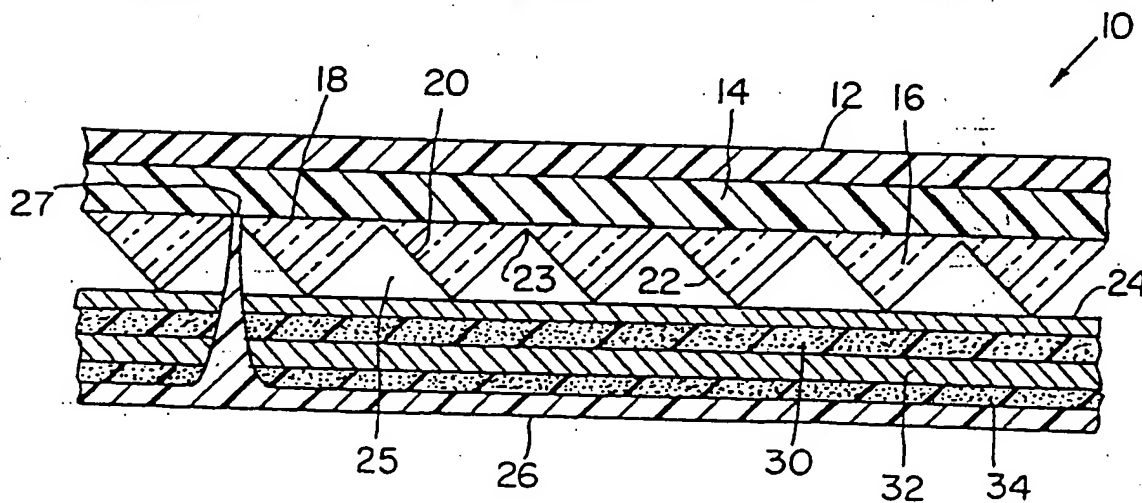


FIG. 3

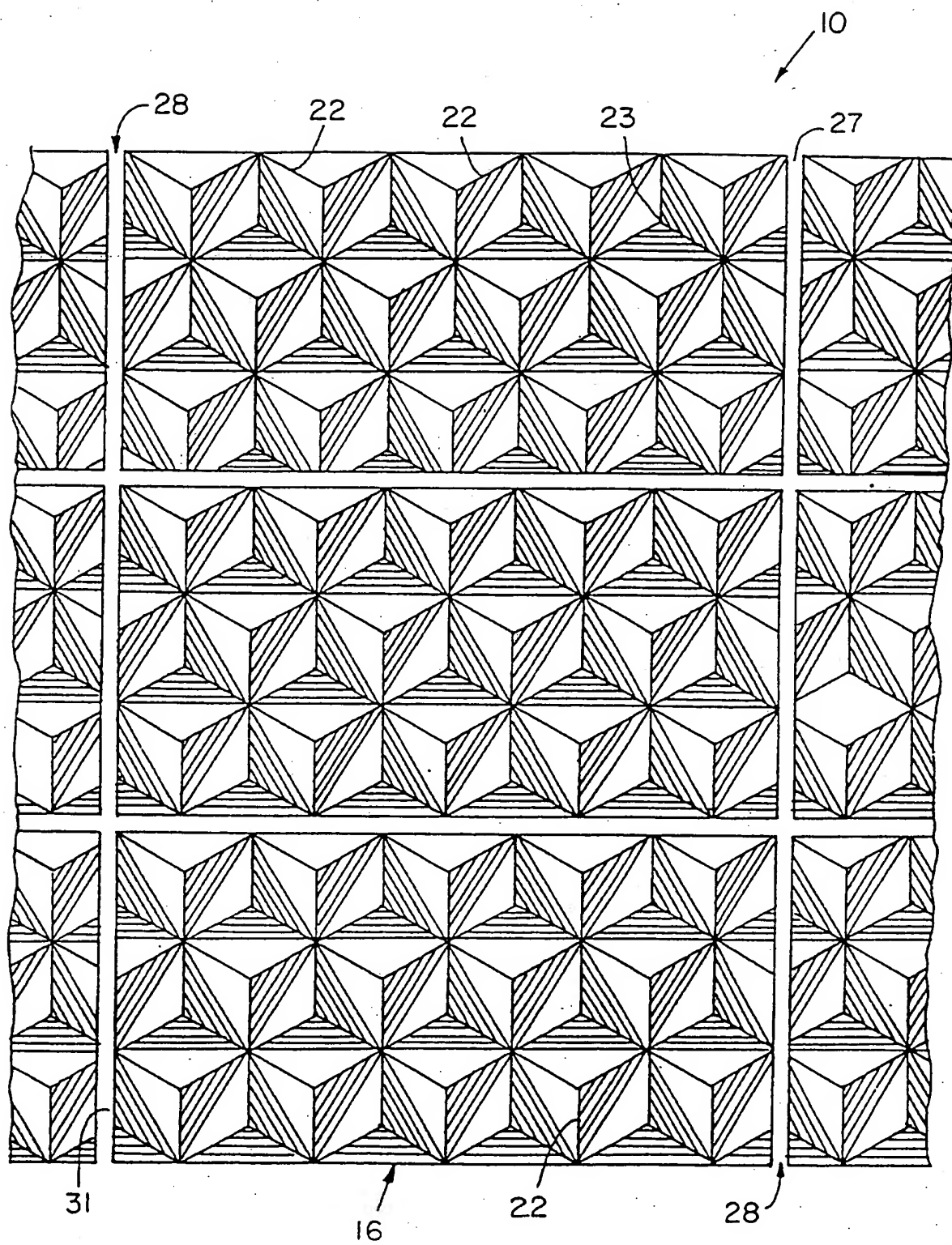


FIG. 1B

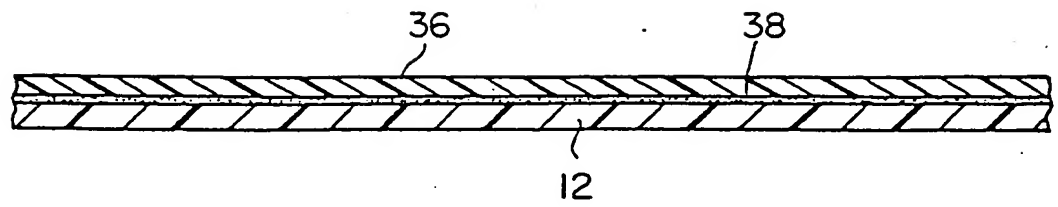


FIG. 4A

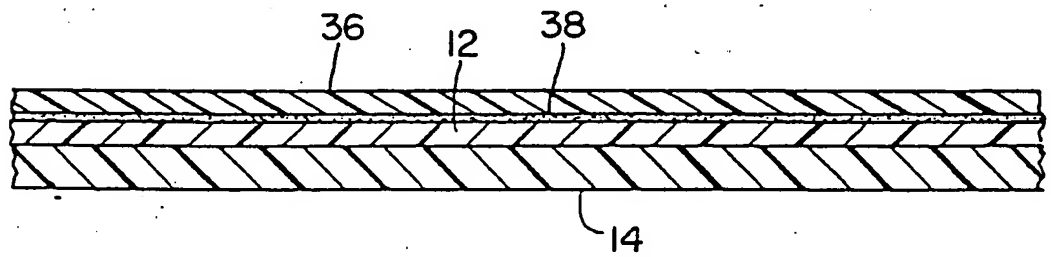


FIG. 4B

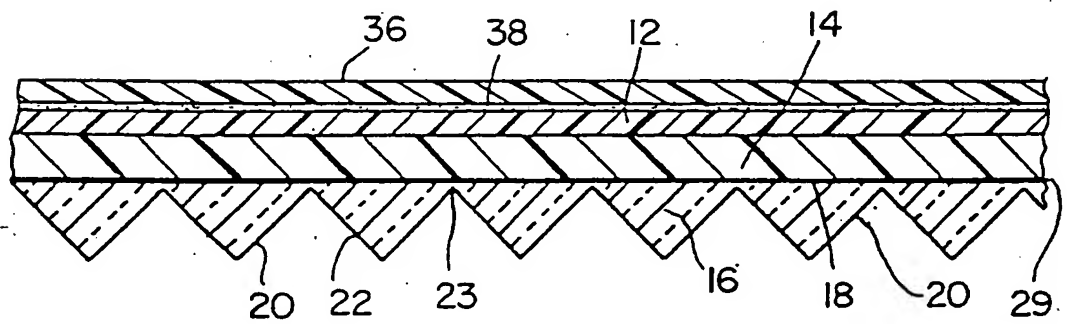


FIG. 4C

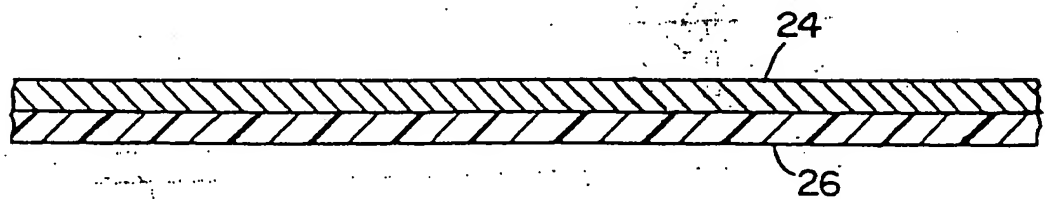


FIG. 4D

4/4

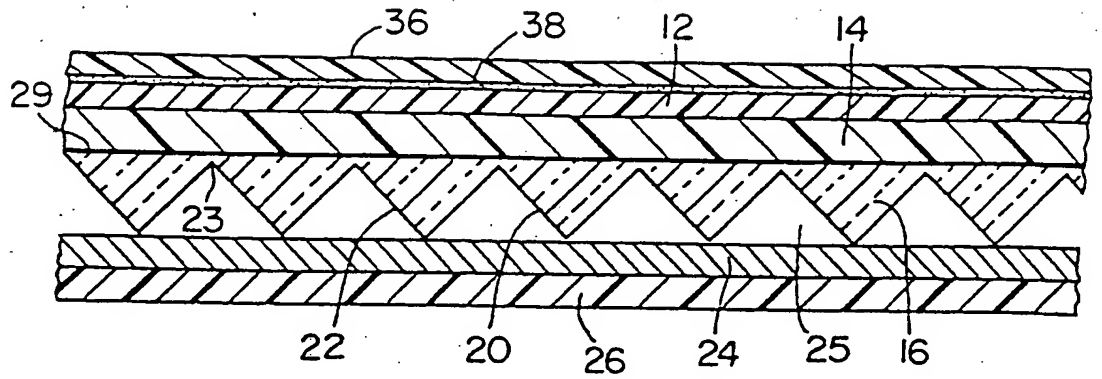


FIG. 4E

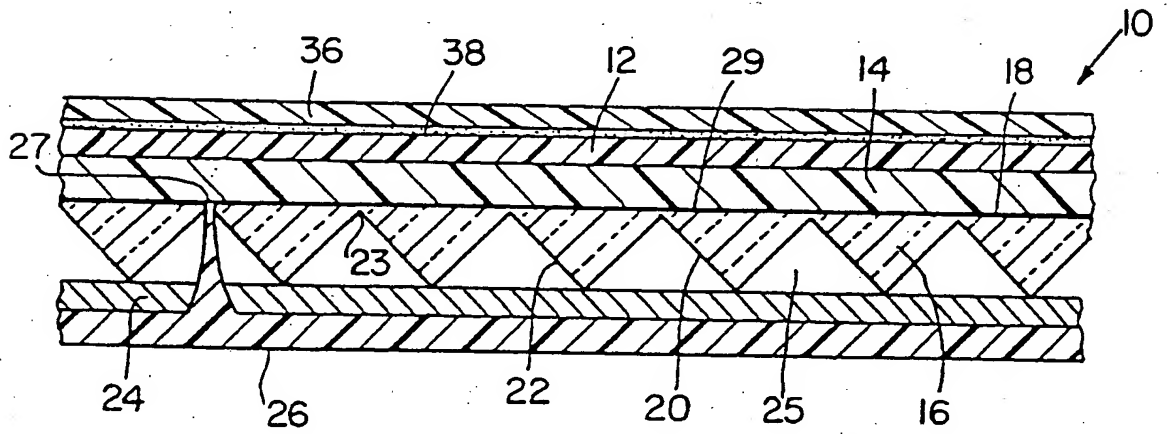


FIG. 4F

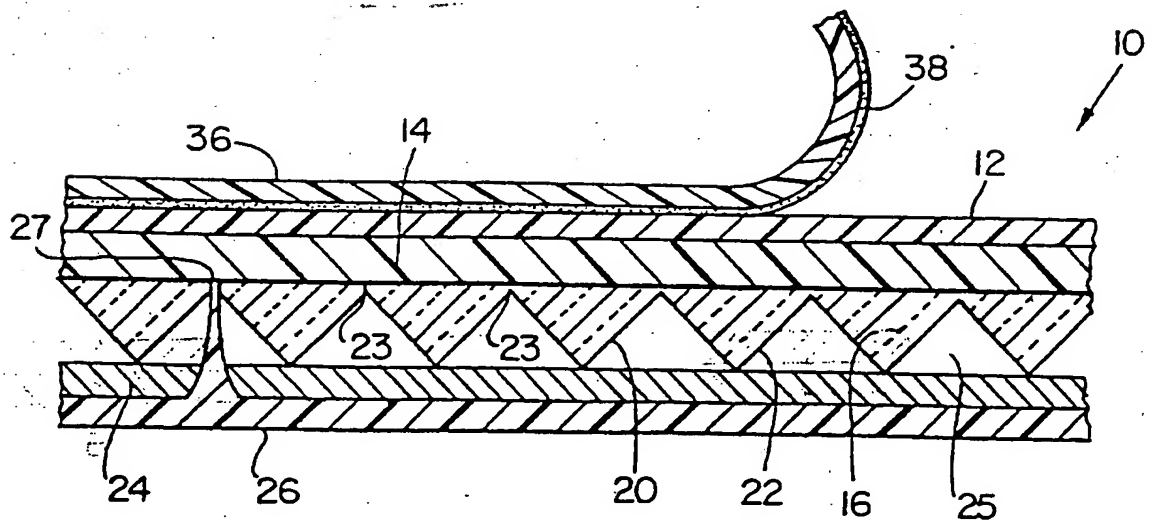


FIG. 4G

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/US 94/10036

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/08 B32B3/28 A62B17/00 G02B5/124

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B A62B G08B A41D G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 171 900 (MINNESOTA MINING AND MANUFACTURING COMPANY) 19 February 1986 see the whole document ---	1,2,4,5, 8,9, 14-18,23
A	EP,A,0 481 634 (MINNESOTA MINING AND MANUFACTURING COMPANY) 22 April 1992 see column 3, line 15 - line 34; figure 2 see column 6, line 30 - line 42 ---	1,10,11, 14,15,23
A	DE,A,31 19 489 (BLUCHER, HUBERT VON) 2 December 1982 see page 9, line 1 - line 21; claims --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "T" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "Z" document member of the same patent family

Date of the actual completion of the international search

19 December 1994

Date of mailing of the international search report

08.12.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Pamies Oille, S

1. The first of these is the fact that the
 2. Government has been unable to obtain the
 3. necessary funds to carry out its policy.
 4. This is due to the fact that the
 5. Government has been unable to obtain the
 6. necessary funds to carry out its policy.
 7. This is due to the fact that the
 8. Government has been unable to obtain the
 9. necessary funds to carry out its policy.
 10. This is due to the fact that the
 11. Government has been unable to obtain the
 12. necessary funds to carry out its policy.

SECRET

4021 73 1-22 . 2

.....

1. The first step is to identify the problem or question that needs to be answered. This involves understanding the context and the specific requirements of the task.

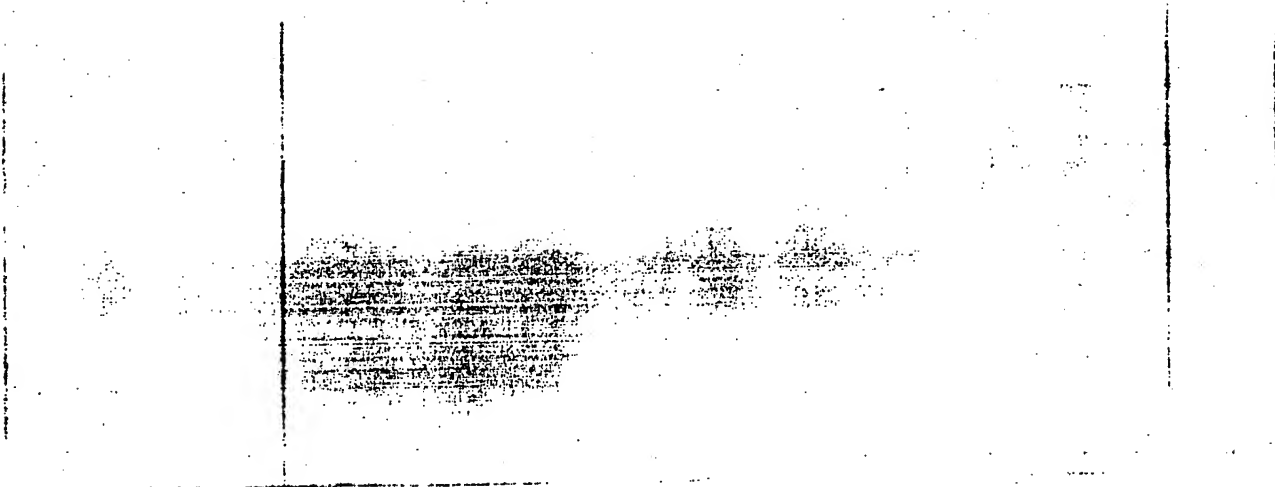
INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/US 94/10036

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 684 348 (ROWLAND) 15 August 1972 cited in the application see column 2, line 11 - line 32 see column 4, line 17 - column 5, line 5 see column 6, line 13 - column 7, line 17 -----	



INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/10036

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0171900	19-02-86	US-A- 4533592	06-08-85
		CA-A- 1230812	29-12-87
		JP-A- 61041101	27-02-86
EP-A-0481634	22-04-92	US-A- 5110655	05-05-92
DE-A-3119489	02-12-82	SE-B- 455478	18-07-88
		SE-A- 8105210	16-11-82
US-A-3684348	15-08-72	DE-A,B,C 2148661	30-03-72
		FR-A,B 2108058	12-05-72
		GB-A- 1355669	05-06-74
		JP-C- 1405928	27-10-87
		JP-A- 55159964	12-12-80
		JP-B- 62013915	30-03-87
		SE-B- 387579	13-09-76
		US-A- 3810804	14-05-74

THIS PAGE BLANK (USPTO)